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MOLECULAR ORDER AND SOLIDIFICATION PROCESSES IN ORGANIC 1/1
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R J JAKOBSEN ET AL. 15 JAN 84 AFOSR-TR-84-0425

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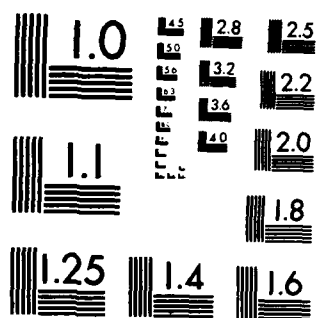
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FINAL SCIENTIFIC REPORT
on
MOLECULAR ORDER AND SOLIDIFICATION
PROCESSES IN ORGANIC LIQUIDS AND
SOLUTIONS

(USAF-OSR Grant 80-0166)

to

UNITED STATES AIR FORCE
OFFICE OF SCIENTIFIC RESEARCH

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BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of this program was to study the behavior of lubricants that are subjected to high temperatures and pressures such as in ball bearing applications. Solutions of organic acids in hydrocarbons were selected as prototype lubricants and a diamond anvil high pressure cell was used for the observations. (microscopic, FT-IR, Raman). SHORT AND LONG RANGE ORDER STUDIES-Past studies have indicated the possibility of aggregation of acid molecules at high, but constant pressure. In order to check this observation, equipment modifications were needed to precisely		

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measure pressures and to rapidly obtain both pressure measurements and infrared spectra. Accordingly, a combination microscope and beam condenser stage for the high pressure cell was constructed. This allowed us to rapidly align the cell and obtain spectra. Also a monochromator and laser were assembled into a system capable of making ruby chip fluorescence measurements. In this technique a tiny ruby chip is placed in the pressure cell, excited with a laser, and the fluorescence measured. The frequencies of the ruby fluorescence can be exactly related to the pressure, in the cell. With this equipment we determined that at high pressure acid aggregation was occurring, as evidenced by a low frequency shift of the acid carbonyl frequency, but the pressure measurements indicated that the pressure was slightly increasing, probably due to gasket extrusion. Thus the increased hydrogen bonding or aggregation was a result of this slight pressure increase. Long range order, in acids, hydrocarbons, and acid-hydrocarbon solutions while under pressure was tested by means of polarized infrared spectra. No changes in the dichroic ratio were detected indicating no evidence of long range order.

~~KINETIC AND REACTION MECHANISM STUDIES~~ When film lubricants, such as in ball bearing applications, are in contact with metal, these metals can interact with organic acids to form organic salts. It has been postulated that these metal salts actually provide the lubrication in such systems. Past work in solutions are in contact with metal. However, in this past work with monocarboxylic acids, no clear evidence of monomer carbonyl infrared bands was observed. Thus the mechanism of reaction appeared to be cyclic dimer acid reacting directly to form acid salt. However, this left open questions about possible intermediate reactions and the observed multiple carboxylate (COO^-) frequencies, which indicate different types of organic salts or different types of acid to metal bonding. In the last phase of this project, numerous temperature studies were carried out in the diamond anvil cell with solutions of lauric acid-dodecane and with the diamond anvils coated with a thin film of iron. With the significant increase in sensitivity from our instrumental developments, these studies showed a small amount of monomer formation at elevated temperatures, as evidenced by a 1767 cm^{-1} . Only after monomer appeared did salt formation commence and then the rate of salt formation appeared to be proportional to the rate of monomer formation, indicating that salt was formed from the monomer. In addition, four distinct carboxylate frequencies were observed to form under various experimental conditions. From the rates of formation, the rates of loss of carbonyl, and the observed frequencies, four separate structures have been deduced for the acid salts.

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MATTHEW J. RAISER
Chief, Technical Information Division

INTRODUCTION

During the course of this program, investigations have been carried out in four areas:

- (1) Kinetic studies of solidification
- (2) Short range order studies
- (3) Long range order studies
- (4) Reaction mechanism studies.

The long range goal of this research was to determine the mechanism of the reaction of organic acids with metals to form organic salts. Such reactions were selected as models or prototypes for lubrication systems, especially thin film lubricants such as in ball bearings where the lubricant is subjected to both high pressures and temperatures.

Previous work in our laboratory (1) had indicated that, under certain conditions, the acid in an acid-hydrocarbon solution (to simulate lubricants) would react with a metal to form organic salts and often the salts were several molecular layers thick. However, this work left three major questions unanswered:

- (1) How did the metal ions move to molecular layers other than the one directly attached to the metal.
- (2) How did the reaction proceed since no monomer carbonyl frequency had been observed in the infrared spectra of this reaction?
- (3) What was the nature of the different types of organic salts formed as evidenced by multiple carboxylate vibrations in the infrared spectra?

At that time, the infrared sensitivity was not such that answers could be provided to these questions, but soon some preliminary studies in our laboratory (2) involving the use of Fourier transform infrared spectroscopy (FT-IR) coupled with the use of a diamond anvil high pressure (HP) cell indicated that needed preliminary information could be obtained in this manner. Accordingly we set out to do the (1) kinetic studies of solidification and the (2) short and (3) long range order studies. In order to provide unambiguous data on these three points we found it necessary to modify and extend the FT-IR-HP technique. When these changes were complete we found out that our preliminary indications of short and long range order were experimental artifacts and no evidence of order could be detected.

(1) R. J. Jakobsen, Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems, Vol. II, J. Ferraro and L. Basile, eds., pp. 165-191, Academic Press, Inc., New York, New York, 1979.

While the ordering studies were unsuccessful, the extension and modifications of the FT-IR-HP technique coupled with improvements in FT-IR hardware and software provided a marked increase in infrared sensitivity. This sensitivity increase indicated that we could proceed directly to the reaction mechanism studies and obtain information that would help answer the three questions about the organic acid to organic salt reactions. Accordingly we devoted much of the last year and a half to the study of such reaction and have obtained information about how the reaction proceeds and about the nature of the different types of organic salts formed.

EXPERIMENTAL MODIFICATIONS

A combination microscope and beam condenser stage for the high pressure cell has been constructed and tested. This is allowing us to visually (via the microscope) monitor the sample while under pressure and to instantly obtain infrared spectra without disturbing the sample. Prior to the use of this stage, we would visually detect a pressure induced change in the sample. Once a change was noted, the pressure cell had to be moved to the infrared instrument, and aligned before spectra could be obtained. Additional changes in the sample could occur either in the elapsed time interval between visual observation and the acquisition of the spectrum, or changes could occur because the sample was physically disturbed while being moved from the microscope to the infrared system. Now we can directly correlate visual and spectral observations. In addition, this stage allows us to quickly align the cell in the infrared optical system and we can take photographs of the sample while under pressure.

It has been known for several years that there is a temperature difference of several degrees between the fixed and moveable pistons of the high pressure cell, during rapid heating, but it was believed that the gradient was much less with slow heating rates and that an equilibrium temperature was eventually established. We found with our high pressure cells that the temperature difference could be as much as 20% (i.e., 20 at 100°C) and that a substantial difference of 10-15% remained even after several hours at the same temperature. Because of the exceptionally high thermal conductivity of the diamond anvils in our cells, this meant the sample under study experienced this temperature gradient directly. Considerable scatter in our melting point data, and some confusing data in both short range order and long range order studies were traced to this temperature gradient. This problem has been solved by using a second heating unit attached as a small external heating pad to the thrust plate that applies force to the moveable piston. By applying through this external heater 70% of the voltage applied to the main internal heater of the cell, the temperature gradient is eliminated and excellent temperature stability is maintained.

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- (2) R. J. Jakobsen, C. J. Riggle, and E. J. Dranglis, *Applied Spectroscopy*, 34, 2, 1980.

During the last part of the first year and initial portions of the second year, a microscope was optically interfaced to the laser Raman spectrometer system which we use for the ruby fluorescence pressure measurement. This accessory provides, for pressure measurement purposes, similar convenience to the microscope-beam condenser developed previously for the infrared spectroscopic studies. We are now able to continually observe the sample during temperature and/or pressure changes with interruptions only for the time necessary for the actual fluorescence measurement (usually 1-2 minutes).

KINETIC STUDIES

Pressure studies were carried out on lauric acid (solid), dodecane, and lauric acid-dodecane solutions. Pressure induced changes were measured for each of the three systems and pressure induced solidification points were determined for dodecane and the solutions.

Temperature measurements were also made on these three systems. During the course of the temperature study of the lauric acid-dodecane solutions, a weak band near 1767 cm^{-1} began to appear when the temperature reached the $50\text{-}60^\circ\text{C}$ range. With increasing temperature this band grew slightly in intensity, but always remained weak in intensity compared to the carbonyl band at 1717 cm^{-1} . Liquid or concentrated solutions of lauric acid at room temperature has a hydrogen bonded cyclic dimer structure. In solution, either dilution or temperature increase should break some of the hydrogen bonds and produce some lauric acid monomer. Dilution of a lauric acid- CCl_4 solution showed a weak band at 1760 cm^{-1} which increased in intensity with further dilution. This temperature and dilution behavior and the observed infrared frequency agree with the frequency values and behavior of non-hydrogen bonded monomer carbonyl frequencies of other acids. Thus the strong 1717 cm^{-1} frequency of lauric acid is the carbonyl frequency of a lauric acid hydrogen-bonded cyclic dimer structure, but the weak 1767 cm^{-1} band can be assigned to the carbonyl frequency of a lauric acid monomer. This observation of a monomer frequency at elevated temperatures gave rise to hopes of determining the role of the acid monomer in the acid to salt reaction mechanism. Further discussion of kinetics will be given in the section on Reaction Mechanisms.

SHORT RANGE ORDER STUDIES

Preliminary studies of cluster formation indicated that aggregation of acid molecules was occurring at constant pressure. This was indicated by a slight shift to lower frequencies of the carbonyl band both during a pressure increase and while the system was held constant at the higher pressure. However, at that time, our pressure measuring capability was relatively insensitive and we could not be certain that small pressure or volume changes (due to gasket extrusion) were not taking place. Therefore, we acquired a suitable monochromator and laser and assembled a system which allows us to measure more exact pressures using the ruby chip fluorescence technique developed by the National Bureau of Standards. In this technique, a tiny ruby chip is placed in the pressure cell (about 5 to 10 percent of the volume of the cell), excited with a laser, and fluorescence spectra obtained with the monochromator. The frequencies of the ruby fluorescence peaks are exactly related to the pressure in the cell.

Using the ruby chip fluorescence technique we can raise the pressure in the diamond cell and monitor the pressure and any changes in the pressure. By using the combination microscope and beam condenser, infrared spectra and pressure measurements can be made every few minutes. In this manner we have determined that even though we thought we were at constant pressure, there was a slight pressure increase with time (probably by gasket extrusion) and that this pressure increase could account for the small infrared frequency shift. At this point it was decided to curtail short range order studies in favor of reaction mechanism studies.

LONG RANGE ORDER STUDIES

The original plans for this portion of the research were based on obtaining polarized infrared spectra of both liquids and solids. This should provide information on the existence of long range order in the polar portions of the acid molecules (the acid carbonyl groups). Acquisition of a Raman spectrometer system prompted us to attempt to adopt the diamond cell technique to the Raman system using a microscope Raman technique. However, our attempts to obtain Raman spectra have not been successful due to a large extent to lack of a suitable detector system.

In addition to the lack of Raman spectra, no order was detected in polarized infrared spectra of acid-hydrocarbon systems.

REACTION MECHANISM STUDIES

Since a monomer carbonyl vibration was detected in heated samples of lauric acid-dodecane solutions in the diamond cell, studies of the acid to salt reaction at high temperatures were emphasized. In experiments with no metal surface present, the lauric acid-dodecane heated solution runs not only:

- (1) showed the appearance of a monomer carbonyl frequency at 1767 cm^{-1} , but also
- (2) showed the appearance of an 1818 cm^{-1} frequency at temperatures somewhat higher than needed for the appearance of the monomer carbonyl band,
- (3) did not show evidence for the formation of acid salt (no bands appeared in the $1520\text{--}1650\text{ cm}^{-1}$ range), and
- (4) often showed high frequency broadening of the 1717 cm^{-1} cyclic dimer acid carbonyl frequency.

The lack of acid salt frequencies was expected since no metal was present in the system but this had to be confirmed before introducing metal into the system.

The nature of the structure giving rise to the 1818 cm^{-1} band is unknown and only speculation is available at the present time. A frequency near 1818 cm^{-1} is too high to be a carbonyl frequency and thus, it is surmised that this must be a combination or overtone band. However, there do not appear to be two bands at the proper frequencies for a combination band. The OH out-of-plane deformation for the cyclic dimer falls at 940 cm^{-1} . Thus its overtone would appear near 1880 cm^{-1} , too high a frequency to fit the 1818 cm^{-1} band. Yet this band at 1818 cm^{-1} appears only at higher temperatures and a temperature increase might weaken the hydrogen bonds - even possibly forming a small amount of a linear dimer. The carbonyl band of a linear dimer should fall between that of the cyclic dimer (1717 cm^{-1}) and that of the monomer (1767 cm^{-1}), but probably nearer to that of the cyclic dimer. Thus the appearance of this band only at higher temperatures along with the high frequency broadening of the 1717 cm^{-1} carbonyl might indicate that the 1818 cm^{-1} band is the first overtone of the OH out-of-plane deformation of a linear dimer. This is also supported by the fact that the symmetries of the linear and cyclic dimers are different and the selection rules might favor the infrared activity of the linear dimer overtone. Also, at higher temperatures, the OH out-of-plane deformation is centered at $925\text{--}930\text{ cm}^{-1}$ making an 1818 cm^{-1} overtone more feasible.

Following these observations, a multitude of temperature experiments were carried out using lauric acid-dodecane solutions in a diamond cell with iron coated (by sputtering) diamond windows. In all these experiments the following three steps occurred:

- (1) At temperatures above 60 C , a monomer carbonyl frequency appeared near 1767 cm^{-1} .
- (2) At temperatures above 80 C , a band at 1818 cm^{-1} appeared.
- (3) In all runs but two, frequencies indicative of organic metal salt formation appeared at temperatures near 100 C . The two runs where no salt formation was detected were the only two runs using fresh iron coated diamond windows.

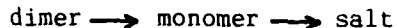
The reason for the lack of salt formation on fresh iron surfaces is not known at this time, but it must have something to do with the nature of the iron oxide surface of fresh iron coatings versus aged iron coatings.

However, in all the runs where organic metal salts (iron laurate) did form, it is apparent that:

- (1) At elevated temperatures some acid dimer breaks apart to form monomer.
- (2) Salt formation was never observed unless the salt formation had been preceded by monomer formation.
- (3) The amount of monomer formed appears to be dependent on the dimer-monomer equilibrium and when this equilibrium is disturbed by salt formation decreasing the monomer concentration, the equilibrium is re-established by more formation of monomer from dimer.

- (4) The rate of salt formation apparently never exceeds the rate of monomer formation and salt formation ends when monomer formation ends.

Thus in our early studies with lower sensitivity no monomer had been observed and the reaction mechanism was therefore unclear even though it was expected that the salt formed from acid monomer. Evidence has been obtained that the reaction mechanism is:

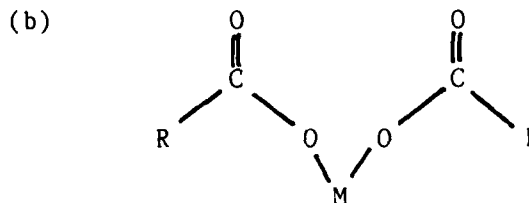
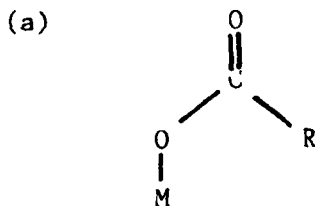


There is also some indication that salt can also form from the linear dimer since it has a free OH end group. This is supported by the rate of formation and loss of the 1818 cm^{-1} band and by the structure of some of the salts formed (to be discussed in the following paragraphs).

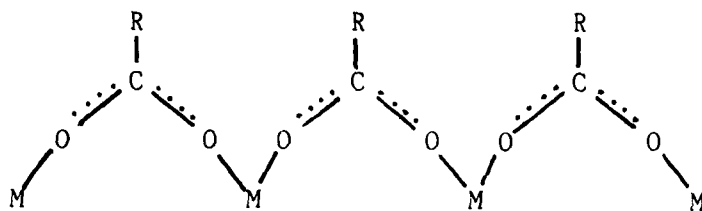
In all of the runs studied, the type and rate of salt formation falls into one of two categories:

- (1) After lengthy periods of time near 100°C there is a small loss of dimer acid carbonyl along with simultaneous observation of acid salt carboxyl vibrations near 1570 and 1615 cm^{-1} . The 1570 cm^{-1} band is generally somewhat stronger than the 1615 cm^{-1} band. Both increase slightly and slowly with time of heating and when the 1570 cm^{-1} band is of sufficient strength a 1550 cm^{-1} shoulder can be observed on this band. When the 1550 , 1570 , and 1615 cm^{-1} bands stop increasing, there is still a major percentage of the dimer acid carbonyl remaining at 1717 cm^{-1} and no free or monomer carbonyl is observed at 1767 cm^{-1} .
- (2) Near 100°C , the appearance of an acid salt carboxyl band at 1530 cm^{-1} is observed followed by a 1550 cm^{-1} band. The 1530 cm^{-1} band appears to remain constant in intensity, but the intensity of the 1550 cm^{-1} band increases very rapidly along with the appearance of a 1570 cm^{-1} band and almost the complete disappearance of the dimer acid carbonyl band at 1717 cm^{-1} .

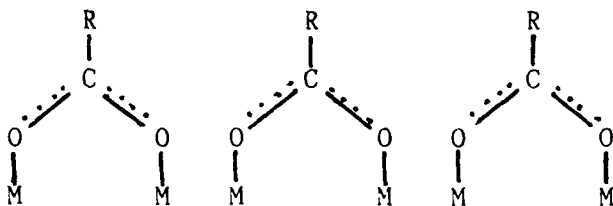
Thus four frequencies (1615 , 1570 , 1550 , and 1530 cm^{-1}) have been observed for asymmetric acid salt carboxylate vibrations indicating four different acid salt structures or bonding to the metal atoms. From the combination of the data on mechanism of formation, rate of formation, relation to monomer and dimer acid carbonyl intensities, and the frequencies of the carboxylate vibrations, the following four structures have been proposed for the metal salts:



(c)



(d)



Although the assignment of frequencies to these structures is not unambiguous, the data best fit the following assignments:

- (a) - 1615 cm^{-1}
- (b) - 1530 cm^{-1}
- (c) - 1570 and 1550 cm^{-1}
- (d) - 1570 cm^{-1}

Thus the diamond cell temperature studies of acid-hydrocarbon solutions did not answer the question concerning metal movement to various salt layers, but did answer questions about the reaction mechanism and the nature of the organic acid salts that were formed.

PRESENTATIONS AND PUBLICATIONS

- o High Pressure Studies of Model Lubricant Systems, J. W. Brasch, C. J. Riggle, E. Drauglis, and R. J. Jakobsen, The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March, 1981.
- o A Beam Condenser Microscope System for High Pressure and General Microsampling, J. W. Brasch and C. J. Riggle, 1981 International Conference on Fourier Transform Infrared Spectroscopy, Columbia, SC, June 1981.
- o High Pressure Spectroscopic Studies of Model Lubricants, J. W. Brasch, E. J. Drauglis, C. J. Riggle, and R. J. Jakobsen, Ohio State Symposium on Molecular Spectroscopy, Columbus, OH, June, 1981.
- o Applications of a Microscope-Beam Condenser Accessory in Model Lubricant Systems and in Polymer Analysis, J. W. Brasch, R. J. Jakobsen, and C. J. Riggle, The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March, 1982.

- o Infrared Spectroscopy of Small Samples Using a Combined Microscope-Beam Condenser System, J. W. Brasch, R. J. Jakobsen, and C. J. Riggle, Annual Conference of the Microbeam Analysis Society, Washington, DC, August, 1982.
- o High Pressure Spectroscopy Studies of Model Lubricant Systems, J. W. Brasch, C. J. Riggle and R. J. Jakobsen, Federation of Analytical Chemistry and Spectroscopy Societies Annual Meeting, Philadelphia, PA, September, 1982.
- o A Combination Microscope-Beam Condenser Accessory for FT-IR Spectrometer Systems, J. W. Brasch, R. J. Jakobsen, and C. J. Riggle; Applied Spectroscopy, submitted for publication.
- o FT-IR Studies of Organic Acid Adsorption and Reaction on Metal Surfaces, R. J. Jakobsen, J. W. Brasch, and C. J. Riggle, Applied Spectroscopy, submitted for publication.

PROJECT PERSONNEL

J. W. Brasch
 E. J. Drauglis
 R. J. Jakobsen
 C. J. Riggle